

Automotive Sulfate Emission Data

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This paper discusses automotive sulfate emission results obtained by the Office of Mobile Source Air Pollution Control of EPA, General Motors, Ford, Chrysler, and Esso. This work has been directed towards obtaining sulfate emission factors for cars with and without catalyst. While the EPA and Chrysler investigations have found significant sulfate formation in noncatalyst cars, GM, Ford, and Esso have found only trace levels from noncatalyst cars. All of these investigators agree that much higher quantities of sulfate are emitted from catalyst cars.

The work done to date shows pelleted catalysts to have much lower sulfate emissions over the low speed-EPA Federal Test Procedures than monolith catalysts. This is probably due to temporary storage of sulfates on the catalyst due to chemical interaction with the alumina pellets. The sulfate compounds are, to a large degree, emitted later under higher speed conditions which result in higher catalyst temperatures which decompose the alumina salt.

Future work will be directed towards further elucidation of this storage mechanism as well as determining in detail how factors such as air injection rate and catalyst location affect sulfate emissions.

Measurement Methods for Automotive Sulfate Emissions

The sulfur in gasoline (about 0.03% by weight) oxidizes to SO_2 in the combustion process with minute quantities of SO_3 also being formed. It is important to note that on a national average SO_2 emissions from motor vehicles are less than 1% of total SO_2 emissions from man made sources. Atmospheric SO_2 is slowly oxidized to SO_3 . However, automotive oxidation catalysts apparently increase the amount of SO_3 directly emitted from motor vehicles and may result in high localized sulfate levels.

Increased sulfate emissions from catalyst equipped vehicles were discovered about a year ago in an analysis by Ford on particulate samples collected by EPA under contract EHS-70-101 with Dow (1). These samples

were collected from a vehicle equipped with an Engelhard noble metal monolith oxidation catalyst. Abnormally high particulate emissions were obtained on this car, even though it was operated with unleaded fuel. Some of the samples were sent to Ford for detailed analysis which showed sulfuric acid to be present. Additional testing confirmed the presence of sulfuric acid. Since this initial finding at the end of 1972, more extensive characterization of sulfate emissions has been done by various groups including the Office of Mobile Source Air Pollution Control (OMASPC) and the Office of Research and Development (ORD) of EPA, General Motors, Ford, Chrysler, and Esso Research. The results of this work, with the exception of the ORD work which is covered in a separate paper, will be summarized in this paper. EPA recently submitted a paper to the Senate Committee on Public Works discussing this project (2).

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The purpose of this work was not only to obtain sulfate emission factors but also to determine what parameters affect sulfate emissions. Parameters that could possibly affect sulfate emissions from catalyst-equipped vehicles include catalyst type (base or noble metal), catalyst substrate (pellet or monolith), catalyst mileage, catalyst location, catalyst operating temperature, and air injection rate. For example, a fresh catalyst with higher activity may result in increased SO_2 oxidation compared to a catalyst with high mileage. Also, catalyst temperature may affect SO_3 formation, since the SO_2 - SO_3 equilibrium shifts more towards SO_2 at higher temperatures.

In addition, to these factors, it is possible to "store" SO_3 on a catalyst by reaction with the alumina-type substrate. This storage could occur in one driving condition, such as low-speed driving, with subsequent release in another condition such as high-speed driving. The high-speed driving results in higher catalyst temperature which would decompose the aluminum sulfates forming at lower temperatures. It is also possible to store and later release SO_2 by similar reactions. This storage and release makes the previous driving history of a catalyst vehicle very important. For example, sulfate emissions obtained over a specified driving cycle from a vehicle previously operated at low speed may be somewhat higher than those on a Federal Test Procedure (FTP) preceded by high speed conditions. Also, it is possible that sulfate would be stored during an FTP to be released later under high speed driving conditions. The work done over the past two years has determined the magnitude of these factors to a preliminary extent.

The work reported has used two basic sampling methods for automotive sulfate emissions; the condensation method by use of a dilution tunnel and the absorption method with the use of an isopropyl alcohol SO_3 scrubber. Most investigators are using the condensation method.

The condensation method uses a dilution tunnel to mix the exhaust in approximately

10:1 proportions with fresh air. A large blower displaces a constant amount of gas mixture including both the entire exhaust volume and whatever volume of dilution air is required at any instant to hold the total amount of gas constant. The exhaust gas and dilution air are mixed in the dilution tunnel, and a small isokinetic sample is withdrawn through a filter, trapping the particulates in the exhaust stream. This method can be used with either a transient driving cycle such as the FTP or a steady-state driving condition. The amount of sulfate collected on the filter is measured either by a wet chemistry technique or by x-ray fluorescence spectroscopy. In this method, SO_2 must be measured independently.

The absorption method has been adapted from one recommended by EPA (3) for measuring SO_3 and sulfate emissions from stationary sources. This method involves passing a small portion (about $0.5 \text{ ft}^3/\text{min}$) of undiluted exhaust gas through either a Greenburg Smith impinger or the smaller type impinger used in the MBTH aldehyde method. The impinger contains an 80% solution of isopropyl alcohol which absorbs both SO_3 and sulfuric acid emissions. The isopropyl alcohol inhibits oxidation of the SO_2 which passes through the impinger. A second impinger in series follows the first one and contains a hydrogen peroxide solution which oxidizes the SO_2 to SO_3 which is absorbed in the solution. This method can be used to measure both SO_3 and SO_2 simultaneously. Since undiluted exhaust gas is sampled, several sampling trains can be set up to simultaneously make measurements before and after the catalyst as well as at the tailpipe. Since this method takes a constant volume of exhaust regardless of the total exhaust flow (which varies greatly under different driving conditions), a sample proportional to the total exhaust can be taken only under steady-state conditions. This method cannot accurately determine sulfate emissions over a transient driving cycle such as the FTP.

Theoretically, it would be possible to sample over a transient driving cycle with

this method using exhaust diluted by a constant volume sampling (CVS) type system. However, it is possible that the much lower level of H_2SO_4 in the diluted exhaust cannot be measured by this method. Still, work will be done to see if the absorption method can be adapted to measure H_2SO_4 levels in dilute exhaust.

General Motors, Ford, and ORD, and OMSAPC (through contract) have used the condensation method. Chrysler, OMSAPC, and, to some extent, GM have used the absorption method. Ford also has used the Goksoyr-Ross method for sulfate measurement which is described later in this paper.

General Motors Work on Sulfates

General Motors has run a number of emission tests on catalyst and noncatalyst cars using the dilution tunnel with both Gelman type A glass fiber filters and nuclepore filters to catch the sulfate emissions. The sulfate was extracted from the filters after the test, reduced to H_2S , and measured colorimetrically by the methylene blue method.

Table 1. GM noncatalyst vehicle sulfate data.*

Vehicle	Fuel sulfur level, %	Test	Sulfates, gpm
1973 Cheverolet	0.02	1972 FTP (8×)	<0.001
1973 Cheverolet	0.15	1972 FTP	0.003
1973 Pontiac	0.04	1972 FTP	0.001
1973 Cheverolet	0.02	60 mph	<0.001
1973 Cheverolet	0.15	60 mph	0.005

* Data of General Motors (4).

GM has tested several different noncatalyst cars for sulfate emissions. These tests showed sulfate emissions of about 0.001 gram per mile (gpm) for fuel of 0.03% sulfate. GM has obtained SO_2 measurements and finds that SO_2 accounts for the remainder of the fuel sulfur. These tests, summarized in Table 1, show that very small amounts of sulfate are formed from noncatalyst vehicles.

A series of tests on seven cars with five different noble metal pelleted oxidation catalysts was also reported by GM. These cars represent the type of system GM will produce in 1975. These vehicles were tested on the 1972 FTP with fuel containing about 0.03% sulfur, approximately the level of current leaded gasoline and slightly higher than unleaded gasoline. The sulfate emissions from these cars are given in Table 2. The sulfate emissions consist of H_2SO_4 , sulfate salts, and perhaps even SO_3 itself. However, sulfate emissions will be reported throughout this report as H_2SO_4 .

The sulfate emissions at 500 miles are 0.007 gpm but have increased to 0.012 gpm at 5000 miles. This may indicate some storage of sulfates on the fresh catalyst due to interaction with the alumina substrate. Possibly at higher mileages, less of the substrate could be available for interaction with the sulfate resulting in increased sulfate emissions. However, it is not possible to draw any firm conclusions on sulfate storage from these data, since the 500 and 5000 mile emissions are from completely different vehicles and different catalysts. The scatter in the emission data on repeat tests is very high.

Table 2. Sulfate emissions from GM catalyst prototypes: 1972 FTP.

Vehicle	Catalyst	Miles	H_2SO_4 emissions, gpm
R3923 1973 Buick	HN 2236	5000	0.014-0.021
R3922 1973 Buick	HN 2236	5000	<0.001-0.010
R3921 1973 Buick	HN 2236	5000	0.010-0.020
R2917 1972 Buick	HN 2079	500	0.004-0.032
R3932 1973 Chevrolet	HN 1290	500	0.001-0.005
BA377 1973 Buick (no air injection)	HN 2364	500	<0.001-0.004
ES83189 1973 Chevrolet	HN 1646	500	<0.001 Avg. 0.009

* Data of General Motors (4)

Table 3. Sulfate emissions from Engelhard monolithic catalysts. *

Vehicle	Catalyst	Miles	H ₂ SO ₄ , gpm
AC32419 1973 Chevrolet	PTX 513 (Type IIB)	500	0.017-0.040
R124 1971 Chevrolet	PTX 5	400	0.030-0.040
Esso 98 1973 Chevrolet	PTX 513	200	0.038-0.043
			Avg. 0.034

* Data of General Motors (4).

However, these data do show that high low-mileage catalytic activity does not result in high sulfate emissions. These tests show an overall average sulfate emission figure of 0.009 gpm over the 1972 FTP which is lower than any other investigators have found.

GM ran similar low-mileage sulfate tests on Engelhard PTX noble metal monolithic oxidation catalysts. The results of these tests are given in Table 3.

These tests show an average of 0.034 gpm of sulfate emission, which is considerably higher than those from the pelleted catalysts in Table 2. Perhaps the monolithic catalyst is not subject to the sulfate storage or inherently has higher activity for SO₂ oxidation.

GM did not obtain SO₂ measurements on many of these tests with catalyst cars, which would have provided a material balance. If the sum of the SO₂ and sulfate emissions were less than the sulfur burned by the engine, this would indicate a sulfate storage phenomenon. In recent work, GM has obtained SO₂ measurements on catalyst cars and concludes that a storage problem may exist.

Recent GM data, informally reported to EPA (5) and given in Table 4 agree somewhat with those reported in Tables 1 and 2. However, GM finds that air injection on pelleted catalyst cars increases sulfate emissions by a factor of five. It is important to note that close control of air injection could be an effective way to control sulfates.

GM ran a limited number of tests by using the absorption method and the condensation method (2). The results of these tests are given in Table 5.

Table 4. Recent GM sulfate data: 1972 FTP.

Vehicle	Sulfates, gpm
Pelleted catalyst, no air injection	0.002
Pelleted catalyst, air injection	0.01
Monolith catalyst	0.02

Table 5. Comparison of absorption and condensation method for sulfates

Catalyst	Driving conditions, mph	Sulfate emissions, gpm Condensation method	Absorption method	
			Before cat.	After cat.
HN 2364	30	0.013	0.009	0.018
	60	0.029	0.019	0.016
	60	0.039	0.006	0.025

These results show poor and erratic agreement between the two methods. These measurements are the only ones taken simultaneously on the same vehicle by both methods. The absorption method shows much higher sulfate emissions before the catalyst than the condensation method shows on non-catalyst cars. For catalyst cars, the absorption method shows higher emissions than the condensation method at 30 mph but lower emissions at 60 mph, indicating no clear trend. Much more work is needed to correlate these methods.

Ford Motor Company Work on Sulfates

Ford analyzed the samples, collected under the EPA contract with Dow, in which sul-

furic acid emissions were first noted as an unregulated automotive pollutant (6). Ford is currently exploring this problem by in-house work and by contract with Battelle Research Laboratories. The Ford program is divided into three phases: phase 1 involves engine dynamometer testing at steady state speeds to develop sampling and analysis methodology, both sulfate and SO₂ emissions being analyzed; phase 2 constitutes obtaining emission data for sulfates and SO₂ from vehicles by using the 1975 FTP; phase 3 is determination of effects of parameters such as catalyst type and age, temperature, oxygen level, and space velocity on sulfate emissions. The mechanism of any sulfate storage phenomenon will be investigated.

Battelle Research Laboratories has done the first phase of the project, with Ford currently doing phases 2 and 3 in-house. The Ford Battelle studies are using both the standard condensation method with a dilution tube and filters and the Goksoyr-Ross method. The Goksoyr-Ross method involves condensing the sulfuric acid from a small stream of undiluted exhaust. The acid is condensed in a glass coil at 60–90°C. The SO₂ passes through the coil uncondensed and is then removed by a hydrogen peroxide solution. The SO₂ sample collection and analysis is identical to that in the absorption method described earlier. The Goksoyr-Ross method, like the absorption method, can only be used for steady-state conditions when concentrated exhaust is used.

Ford has only preliminary results to date on an engine dynamometer for sulfate emissions and has no SO₂ data to determine a material balance. The results to date (7) are given in Table 6 for fuel containing 0.031% sulfur.

The Ford work investigated where the sul-

fate originated in the catalyst-equipped engine and found it first appeared across the catalyst itself. Ford has also determined that about 90% of the sulfate particulates are less than 0.3 μ m in diameter.

Chrysler Corporation Work

Chrysler Corporation has done extensive measurement of sulfate emissions from both catalyst and noncatalyst cars by use of the absorption method. Chrysler has also done considerable work justifying use of this method. Both areas will be discussed in the following sections.

Chrysler Work on Method Development

Chrysler has used the absorption method for all of their work. This method involves bubbling a small portion of undiluted exhaust directly into a small impinger, the same type used in the MBTH aldehyde measurement method, filled with an 80% solution of isopropyl alcohol. The SO₃ and sulfates are measured by titration. Chrysler measured the SO₂ directly with a DuPont Model 411 SO₂ analyzer. Chrysler did all of its measurements by a hot start 1975 FTP. As mentioned earlier, it is not valid to use this type of sampling system, which takes a small sample of undiluted exhaust at a constant flow rate, in a transient driving cycle. A transient driving cycle gives various exhaust flow rates which would result in a sample not proportional to the actual emissions. However, the belief at Chrysler is that this sampling system is valid for indicating trends in sulfate emissions. Chrysler feels that SO₃ or sulfate samples can be taken directly from a bag using the standard CVS-FTP test and is investigating this possibility. If sulfates can be measured this way, the nonproportional sampling problem will be solved.

Chrysler did extensive work on establishing the validity of this method. The initial work was done in a tube furnace containing catalyst samples and showed substantial formation of SO₃ over a catalyst. Samples of

Table 6. Sulfate emissions at 60 mph.

Control system	H ₂ SO ₄ , gpm
Catalyst	0.05
Noncatalyst	0.001

SO₂ and O₂ passed through the tube furnace at 1000°F showed no sulfate being formed. However, exhaust components such as nitrogen oxides may affect SO₂ oxidation in the sampling systems. Chrysler passed a mixture of SO₂, O₂, H₂O, NO, and CO through the empty tube furnace at 1100°F and other temperatures to address this point and found no SO₃ (8).

In addition to the tube furnace work, Chrysler has done additional tests with a single-cylinder engine to justify the method. An engine test was run with isooctane fuel containing no sulfur to see if nonsulfur exhaust components will give a positive SO₃ reading. Again, no SO₃ response was noted. Chrysler then introduced some SO₂ into the exhaust system with the engine presumably operating on isooctane fuel which would check whether other exhaust components result in SO₃ formation. About 5% of the SO₂ was converted to SO₃ indicating formation of SO₃ in either the exhaust or sampling system (9). Chrysler reported another test where SO₂ and nitrogen were introduced into the exhaust system of the engine running on isooctane fuel. No SO₃ was found in this test, probably because of the lower oxygen levels than in the preceding test. However, Chrysler reported another test in which SO₂ was introduced into the exhaust system of the engine running on isooctane fuel with no SO₃ being found (8).

Chrysler also did an experiment in which SO₂ was introduced into the sample probe which was at full operating temperature with the engine running on isooctane fuel. No SO₃ was found. Chrysler then introduced SO₂ into the impinger itself with the engine running on isooctane fuel and found no SO₃. Chrysler did a third experiment in which particles from the exhaust systems, presumably iron type compounds were added, and the impinger solutions was titrated without any exhaust being passed through the system. The titration showed no SO₃ to be present, demonstrating that exhaust particles by themselves do not give a positive SO₃ reading. Chrysler then ran a sample of engine

exhaust from a sulfur containing fuel through the impinger system with exhaust system particles in the impinger. The amount of SO₃ was 60% less than that found without the exhaust system particles in the impinger. This indicates that exhaust system particles somehow react with the SO₃, possibly by absorption (8).

Chrysler has run several single cylinder engine tests with a catalyst in the system and, in all cases, found increased SO₃ formation over the catalyst. These tests involved measuring sulfate emissions from CVS bags identical to those used for HC, CO, and NO_x emissions. This involves dilution of the exhaust by a CVS type system which is the first time the absorption method has been used for dilute exhaust. In one of these tests with 0.4% sulfur fuel, 120 and 240 ppm of SO₃ were found before and after the catalyst, respectively. Another single cylinder engine test using 0.4% sulfur fuel, which would give 265 ppm of SO₂ if no SO₃ was present, showed 63 ppm SO₃ before the catalyst and 77 ppm SO₃ after the catalyst.

Chrysler Vehicle Tests

Chrysler has conducted extensive vehicle tests using the absorption method over a hot start 1975 FTP type test. The emission numbers were obtained by the absorption method over a transient driving cycle and are not accurate emission numbers. However, the emission numbers from the Chrysler vehicle tests are believed to be indicative of trends in sulfate emission with various control systems.

Chrysler has tested a large number of non-catalyst cars and, contrary to the results of other investigators, has found substantial sulfate emissions. Six 1975 noncatalyst prototypes, two with air pumps and four running lean, were tested with both leaded and unleaded fuel. One 1973 production car was tested with leaded and unleaded fuel. The sulfate emission results and sulfate formed are listed in Table 7 (9,10).

These results show slightly less than 20% conversion to sulfate for noncatalyst cars

Table 7. Sulfate emission data from noncatalyst vehicles by modified 1975 FTP.

Vehicle	Fuel sulfur level, %	Lead level, g/gal	H ₂ SO ₄ emissions, gpm	S converted to H ₂ SO ₄ , %
Car 185, 1975 prototype				
Air pump on	0.1	0	0.13	16
Air pump off	0.1	0	0.20	18
Air pump on	0.012	3.2	0.009	9
Car 294, 1974 production	0.014	0	0.013	17
Car 394, 1975 prototype (lean)	0.1	0	0.15	15
Car 588, 1975 prototype (lean)	0.034	2.2	0.016	6
Car 403, 1975 prototype (air pump)	0.014	0	0.031	25
Car 775, 1975 prototype (Ethyl lean reactor)	0.1	0	0.14	16
Car 612				
1973 production car	0.014	0	0.017	14
No air pump	0.027	1.6	0.01	5

Table 8. Sulfate emission data from Chrysler catalyst vehicles by modified 1975 FTP.

Vehicle	Fuel sulfur, %	H ₂ SO ₄ emissions, gpm	S con- verted to H ₂ SO ₄ , %
Car 411, 1975 monolith catalyst (0 miles)			
Before catalyst	0.1	0.20	23
After catalyst	0.1	0.29	34
Car 554, 1975 pelleted catalyst*			
0 miles	0.014	0	0
200 miles	0.014	0.017	13
400 miles	0.014	0.023	19
20,000 miles	0.014	0.012	10

* Four different catalysts.

using unleaded fuel. Less than 10% conversion to sulfate occurs when leaded fuel is used. Leaded fuel results in the formation of some lead sulfate which may not be measured by the absorption method due to its low solubility. The lead sulfates may also be stored temporarily in the exhaust muffler. However, it is significant that leaded fuel shows lower sulfate formation than unleaded fuel.

The percentage of fuel sulfur converted to sulfate was usually determined by the amount of SO₃ and SO₂ found in the exhaust rather than comparing the amount of SO₃ with that found in the fuel. Frequently, the total amount of sulfur recovered was greater than the amount theoretically burned in the engine. This is the reason why SO₃ emissions can be substantially higher in one case (e.g., car 185 with air pump on versus air

pump off) with no change in per cent sulfates and SO₂. A large part of this problem is probably due to the sampling method used. It is also conceivable that sulfates (e.g., iron sulfates) could be stored in the muffler in one driving condition and emitted in another. At any rate, much more work is needed on the sulfur balance to make firm conclusions.

Chrysler has also measured sulfate emissions from a number of vehicles with pelleted and monolithic oxidation catalysts. The results of these tests are given in Table 8 (11).

These results show that a catalyst causes increased SO₂ oxidation but that a significant amount of SO₃ exists before the catalyst. The Chrysler tests are the only tests other than the OMSAPC tests of EPA which show a significant amount of sulfate from noncatalyst vehicles. More work is clearly needed to determine whether this is an actual phenomenon or whether this is caused by errors in the measurement method.

Esso Research and Engineering Work

Esso Research and Engineering has done extensive work on measuring sulfate emissions from catalyst vehicles. Esso has done considerable work developing sampling procedures for sulfates. Their dilution tube has provisions to dehumidify and chill incoming air which prevent water condensation which is not done with other dilution tubes. Esso measured sulfate emissions by the condensation method using this dilution tube for 40

Table 9. Esso Research and Engineering sulfate data.

Vehicle	Driving conditions	Fuel sulfur, %	Sulfate emissions, gpm	Sulfate formation, %
1973 noncatalyst vehicles	1972 FTP	0.040	<0.007	<2
	40 mph	0.067	0.0009	0.2
	40 mph	0.067	0.0040	0.1
	40 mph	0.067	0.0015	0.4
Monolithic catalyst-equipped vehicle	1972 FTP	0.067	0.119	21
	1972 FTP	0.032	0.064	24
	1972 FTP	0.004	0.010	29
	40 mph	0.067	0.158	28
	40 mph	0.032	0.055	20
	40 mph	0.004	0.008	35
Monolithic catalyst-equipped vehicle	1972 FTP	0.067	0.145	25
	1972 FTP	0.032	0.061	23
	1974 FTP	0.004	0.014	41
	40 mph	0.067	0.090	16
	40 mph	0.032	0.048	17
	40 mph	0.004	0.005	18
1975 GM catalyst prototype	1975 FTP	0.065	0.029	5
	1975 FTP	0.065	0.038	7
	1975 FTP	0.034	0.013	4
Pelleted catalyst-equipped vehicle	1975 FTP	0.140	0.11	11
	1975 FTP	0.065	0.036	6
	1975 FTP	0.056	0.015	3
	1975 FTP	0.034	0.011	4
	1975 FTP	0.004	0.003	8
Pelleted catalyst-equipped vehicle	40 mph	0.065	0.049	13
	40 mph	0.034	0.009	5
	60 mph	0.140	0.313	36
	60 mph	0.056	0.113	32
	60 mph	0.032	0.063	28
	60 mph	0.004	0.007	26

mph steady-state and FTP conditions. Esso measured only sulfate emissions and did not measure SO₂ emissions. The Esso emission data are given in Table 9 (12,13) as sulfuric acid (gpm).

The Esso data involved multiple tests for each of the results in Table 9, which were very repeatable. These data show almost no sulfate emissions from noncatalyst cars and significant sulfate from a monolithic catalyst car. Sulfate emissions are present for the GM catalyst car but at much lower levels than for the monolithic catalyst. Since Esso did not measure SO₂, it is not known whether all of the sulfur burned in the engine was emitted or some sulfates are stored on the catalyst by interaction with the alumina substrate. Future work is needed to resolve this point.

EPA Test Results

Both the OMSAPC and ORD have done extensive work measuring sulfate emissions. The OMSAPC in-house work has measured sulfate emissions on five vehicles: Ford-Engelhard catalyst; 1975 GM noncatalyst prototype; 1975 GM catalyst prototype; Gould dual catalyst vehicle; Opel diesel. Only limited measurements were taken on the last two vehicles. ORD has done sulfate emissions measurements on three vehicles: Chrysler car 333, Engelhard catalysts; Ford, Engelhard catalysts; 1975 GM catalyst prototype. In addition to this work, OMSAPC is supporting a contract effort at Dow to measure catalyst particulates. The OMSAPC Dow contract has measured sulfate emissions on four vehicles to date: Ford, Engelhard catalysts (same vehicle tested by OMSAPC in-house); Peugeot diesel; Mazda rotary; Williams gas turbine. The OMSAPC results are covered in this paper while the ORD results are covered in a separate paper. Both OMSAPC and ORD have planned extensive additional work in this area.

EPA-OMSAPC Work With Absorption Method

OMSAPC has obtained extensive emission data with the absorption method which involves sampling a small portion of undiluted exhaust with a quartz probe. The exhaust is bubbled through three impingers in series containing an isopropyl alcohol in the first impinger to absorb SO₃ sulfates and a hydrogen peroxide solution in the second and third impingers to absorb SO₂.

These tests were run at three steady-state speeds, 10, 30, and 60 mph, but could not be run with a transient cycle such as the FTP using concentrated exhaust.

Of the five cars tested by this method, three vehicles were tested extensively. These three cars, conventional engine 1975 prototypes, were: 1975 Ford prototypes, air injection, quick-heat intake manifold, Engelhard catalysts (two sets); 1975 GM noncatalyst proto-

type, exhaust manifold air injection; 1975 GM catalyst prototype, 0-mile noble metal pelleted oxidation catalyst (0.05 oz noble metal), no air injection. The Ford vehicle was tested separately with two sets of Engelhard catalysts. One set had been run 50,000 miles while the second set had less than 500 miles. This vehicle was also tested without a catalyst. Limited tests were done on the two additional cars: a Gould dual-catalyst car, Gould Monel reduction catalyst and noble metal pelleted oxidation catalyst (0 miles on reduction catalyst, 12,000 miles on oxidation catalyst) and an Opel diesel.

All of the OMSAPC tests have several limitations which must be noted. The reproducibility from test to test was very poor. While multiple tests were used to obtain average emission values, the reasons for the poor reproducibility should be understood so this problem can be corrected. The analytical method does not recover all of the sulfur compounds since the material balance is less than 100%. The material balance is poorer for the catalyst vehicles than for the non-catalyst vehicles but is variable for all vehicles. Clearly, much more work is needed to validate this method for mobile sources as it has been validated for stationary sources. Also, work is needed to compare emission results from this method to those obtained by the condensation method. Nevertheless, these test results do give preliminary emission estimates and trends. The emission results for the individual tests are given in an internal EPA report (14,15). This paper reports the average values.

The Ford vehicle was tested with high and low sulfur fuel containing 0.085% and 0.017% sulfur, respectively (12). The test results were interpolated to give an emission estimate for a 0.03% sulfur fuel, assuming a linear relationship between fuel sulfur level and sulfate emissions. It should be remembered that other problems with the measurement method probably resulted in greater errors than introduced by assuming this linear relationship.

Table 10 gives the results of the Ford tests for the vehicle in the following three configurations: no catalyst; fresh catalyst; 50,000 mile catalyst.

The conversion to sulfate was based on the ratio of sulfate and SO₂ found in the test. The sulfur recovered was based on comparing the SO₂ and sulfate found with the sulfur consumed by the engine.

The tests on the Ford vehicle showed the following. There is significant formation of sulfates (over 10% of the fuel sulfur is converted to sulfates) without a catalyst. A catalyst significantly increases sulfate formation (about 20–80% of the fuel sulfur is converted to sulfates). The amount of sulfate formed is about twice as great with a fresh catalyst as with an aged catalyst (50,000 miles). Sulfate emission values are a maximum at 10 mph and a minimum at 60 mph steady-state speeds. This could possibly be due to the lower catalyst temperature (750°F) at 10 mph versus 60 mph (1050°F). The equilibrium conversion to sulfate decreases at higher temperatures.

Table 10. EPA Method 8 Test on Ford vehicle.

Vehicle configuration	Speed, mph	Sulfate, gpm	SO ₂ , gpm	Conversion to sulfate, %	Sulfur recovered, %
No catalyst	10	0.06	0.15	31	102
	30	0.02	0.07	22	97
	60	0.01	0.06	21	74
Fresh catalyst	10	0.16	0.02	96	56
	30	0.10	0.02	83	98
	60	0.03	0.03	45	73
50,000 mile catalyst	10	0.09	0.14	32	97
	30	0.04	0.05	36	87
	60	0.01	0.05	20	66

Table 11. EPA test on 1975 GM prototype noncatalyst vehicle, air pump disconnected.

Probe location	Speed, mph	Sulfate, gpm	SO ₂ , gpm	Conversion to sulfate, %	Sulfur recovered, %
Before muffler	10	0.09	0.15	27	86
	30	0.01	0.05	14	78
	60	0.02	0.11	8	104
At tailpipe	10	0.03	0.17	12	79
	30	0.01	0.04	11	68
	60	0.008	0.09	5	80

Table 12. EPA test on 1975 GM prototype noncatalyst vehicle, air pump connected.

Probe location	Speed, mph	Sulfate, gpm	SO ₂ , gpm	Conversion to sulfate, %	Sulfur recovered, %
Before muffler	10	0.06	0.14	22	78
	30	0.008	0.04	11	65
	60	0.02	0.09	10	84
At tailpipe	10	0.02	0.15	8	71
	30	0.006	0.04	8	60
	60	0.009	0.09	5	82

Table 13. EPA tests on 1975 GM catalyst prototype.

Probe location	Speed, mph	Sulfate, gpm	SO ₂ , gpm	Conversion to sulfate, %	Sulfur recovered, %
Before catalyst	10	0.03	0.15	12	97
After catalyst		0.07	0.009	84	29
At tailpipe		0.07	0.04	52	48
Before catalyst	30	0.009	0.05	8	77
After catalyst		0.04	0.02	63	46
At tailpipe		0.04	0.01	65	40
Before catalyst	60	0.02	0.10	10	101
After catalyst		0.10	0.06	51	112
At tailpipe		0.08	0.06	43	100

The tests on the GM vehicles were more extensive than the Ford tests. Sulfate emissions were usually sampled at the three locations: behind the exhaust manifold before any catalyst present, immediately behind the catalyst in the exhaust system (or behind the reduction catalyst in a dual catalyst system), and at the tailpipe.

Tests were made on a 1975 noncatalyst prototype with the air pump operating and with the air pump disconnected. Tests were also made with a 1975 catalyst prototype with a fresh pelleted noble metal catalyst in the underfloor converter. This vehicle did not have an air pump. The GM test results are given in Tables 11-13. Fuel containing 0.03% sulfur was used in these tests.

The following conclusions can be made from these tests: Significant sulfate emissions

were again found in the noncatalyst vehicle. The sulfate emissions were slightly higher in the noncatalyst car with the air pump running than with the air pump disconnected. Sulfate emissions with the catalyst car were significantly higher than for the noncatalyst car with much of the sulfate being formed over the catalyst itself. Sulfate emissions were higher at 10 mph than at 30 mph. This could possibly be due to the lower catalyst temperature (750°F versus 770°F) at 10 mph. Sulfate emissions are very high at 60 mph and are somewhat greater than at 10 mph. This would not be predicted from thermodynamic considerations since the high catalyst temperature at 60 mph (1120°F) should result in lower sulfate formation. However, the pelleted catalyst may be storing sulfates formed at lower

speeds and releasing them at higher speeds with the higher temperatures. The pelleted catalyst, with the large amount of alumina substrate, probably has a much greater tendency to store sulfates at lower temperatures. This storage results from chemical interaction with the substrate forming sulfate salts which are decomposed at higher temperatures. Such storage has been found occurring with pelleted catalysts from tests run by Esso Research and Engineering.

The test on the Gould dual catalyst car is the first sulfate test reported on a car equipped with a nitrogen oxide reduction catalyst. Duplicate tests were run at 10 and 30 mph. The tests showed some sulfate formation (16 and 30% for 10 and 30 mph, respectively) in the engine and exhaust manifold. The sulfate conversion increased to 50–60% after the reduction catalyst. The sulfate formation was higher yet (78 and 93% at 10 and 30 mph, respectively) at the tailpipe, suggesting additional sulfates were formed in the oxidation catalyst and/or exhaust system. The overall sulfate emissions were about the same levels as those of the GM catalysts.

The Opel diesel vehicle tested had a very small amount of the fuel sulfur (less than 5%) converted to sulfates in the limited tests at 60 mph done by OMSAPC. Even with the sulfur content of diesel fuel being about ten times greater than gasoline, the sulfate emissions are about the same as from a spark ignition engine. However, the SO₂ emissions are much greater than from a conventional engine.

OMSAPC Work with Condensation Method

To date, the OMSAPC work on the condensation method has been limited to that done under contract with Dow Chemical Company (Contract 68–01–0480). Dow has measured particulate emissions on ten types of vehicles (16). Honda CVCC, 1973 Opel diesel, Peugeot diesel, Mazda rotary, Williams gas turbine, Ford with Engelhard 50,000-mile catalyst (vehicle 24A51), Ford with Engel-

hard 0-mile catalyst (vehicle 24A51), GM catalyst prototype (Pontiac) with Monsanto base metal pelleted catalyst, Ford with catalyst (vehicle A342–35), and Capri stratified charge.

Particulate samples for these tests were collected on filters and sent, for the most part, to ORD for sulfate analysis by x-ray fluorescence. Values of SO₂ emissions and sulfur were not obtained on these tests but will be obtained in some of the future tests. Sulfate emission values have been determined for the samples given in Table 4 (16).

These results show that diesel engines to form measurable amounts of sulfate. Sulfate emissions are also found at lower levels for the Mazda rotary and Williams gas turbine.

Conclusions and Planned Future Work

Noncatalyst cars with conventional internal combustion engines have very definite sulfate emissions but at very low levels according to most work. Data from EPA–ORD, GM, Ford, and Esso show sulfate emissions to be about 0.001 gpm or less than 1% of

Table 14. Sulfate emissions for vehicles tested at Dow.

Vehicle	Driving cycle	Fuel sulfur, %	Sulfate, gpm
Ford 24A51, 50,000-mile Engelhard catalyst	1975 FTP (glass fiber filter)	0.03	0.012
	1975 FTP (millipore filter)	0.03	0.022
Ford 24A51, 0-mile catalyst	1975 FTP (glass fiber filter)	0.03	0.014
	1975 FTP (millipore filter)	0.03	0.023
Pontiac, Monsanto base metal pelleted catalyst	1975 FTP (millipore filter)	0.03	0.010
Chevrolet, pelleted catalyst (tested previous to Contract 68–01–0480)	1975 FTP	0.03	0.011
Peugeot diesel	1975 FTP (millipore filter)	0.35	0.009
Mazda rotary	1975 FTP (millipore filter)	0.03	0.003
Williams gas turbine	1975 FTP (millipore filter)	0.03	0.005
	50 mph (millipore filter)	0.03	0.004

the fuel sulfur with the remainder of the fuel sulfur forming SO₂. However, tests by Chrysler and very preliminary EPA-OMSAPC tests show much higher sulfate emissions from noncatalyst cars, about 10-20% of the fuel sulfur being converted to sulfate. However, these tests were made by a different measurement method which has not been sufficiently validated for mobile sources. Overall, the bulk of available data show very low sulfate emissions from non-catalyst cars.

Substantial work has been done by industry to obtain emission factors for sulfates from catalyst equipped vehicles. Work by Chrysler shows very roughly about 10% more fuel sulfur is converted to sulfates with catalysts than without catalysts. Work by GM, Ford, and Esso leads to the conclusion that pelleted catalysts have substantially lower sulfate emissions than monolith catalysts over the EPA Federal Test Procedure. However, preliminary data also show that at higher speeds that both catalysts have similar sulfate emissions. This is probably due to sulfates being stored on the pelleted catalyst at lower speeds and temperatures which are later emitted at higher speeds and temperatures. The monolith catalyst with much less alumina in it probably does not have this storage capacity. Emission factors obtained with 0.03% sulfur fuel, the current national average, are listed in Table 15.

These numbers indicate the EPA estimate of 0.05 gpm published in the previous position paper (2) may be somewhat high.

The sulfate emissions from 1975 type systems designed to meet the interim standards

may be lower than this. For one thing, unleaded fuel will probably have an average sulfur content lower than the current 0.03% for all gasoline. Secondly, more recent GM work indicates that sulfate emissions from cars designed to meet the 1975 interim standards are about 0.002 gpm instead of 0.009 gpm. These recent GM data also indicate that sulfate emissions for GM systems designed to meet the original 1975 statutory standards are about five times higher at 0.01 gpm.

Future EPA-OMSAPC work is planned to obtain additional characterization data and also to assess control technology approaches for sulfates. Various factors on catalyst equipped cars which might result in lower sulfate emissions are: catalyst formulation, air injection rate, and catalyst temperature as affected by catalyst location.

This future EPA-OMSAPC work will be done both in-house and by contract.

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Table 15.

Investigator	Catalyst	Driving cycle	Sulfate, gpm	Sulfate, %
GM	Pellet	1972 FTP	0.009	
GM	Monolith	1972 FTP	0.03	
Esso	Pellet	1975 FTP	0.01	4
Esso	Monolith	1972 FTP	0.06	24
Esso	Pellet	60 mph	0.06	
Ford	Monolith	60 mph	0.05	

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